



Research Article

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## Studies On Interaction Between Cu (II), Cr (II), Nd (III) and Pr (III) Metal Ions And Substituted Hydroxy Chalcones At 0.1 M Ionic Strength pH Metrically

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### ABSTRACT

The interactions of Cu(II), Cr(II), Nd(III) and Pr(III) metal ions with 1(2'-hydroxy-5'-methylphenyl)-3-phenyl Chalcone ( $L_1$ ) and 1(2'-hydroxy-5'-methylphenyl)-3-(4'-methoxyphenyl)-Chalcone ( $L_2$ ) have been substituted at 0.1 M ionic strength in 70 % Dioxane-water mixture by Bjerrum method as adopted by Calvin and Wilson. It is observed that Cu (II), Cr (II), Nd (III) and Pr (III) metal ions form 1:1 and 1:2 complexes with ligands ( $L_1$  &  $L_2$ ). The data obtained were used to estimate and compare the values of proton-ligand stability constant ( $pK$ ) and metal-ligand stability constants ( $\log k$ ). From estimated data ( $pK$  and  $\log k$ ), the effects of substituents were studied.

**Key words:** Substituted hydroxy Chalcones, dioxane-water mixture.

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### INTRODUCTION

Considerable research work has been done in the past, on the study of complexes [1, 2]. The studies in metal-ligand complexes in solution of a number of metal ions with carboxylic acids, oximes, phenols etc. would be interesting which throw light on the mode of storage and transport of metal ions in biological kingdom. With the view to understand the bi-inorganic chemistry of metal ions, Banerjee et al [3] have synthesized a number of mixed-ligand alkaline earth metal complexes. Bjerrum's [4] dissertation has taken the initiative to develop the field. Metal complexation not only brings the reacting molecules together to give activated complex [5] but also polarized electrons from the ligand towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change value. Bulkier group increases the basicity of ligands as well as stability. The stability of complexes is determined by the nature of central metal atom and ligands. The stability of complexes is influenced by the most important characteristics like degree of oxidation, radius and electronic structure. Irving and Williams [6] had studied the order of stability of metal complexes of transition metal ions by comparing the ionic radius and second ionisation potential of metal ions, as it is valid for most nitrogen and oxygen donor ligands. Narwade et al [7] have investigated metal-ligand stability constants of some lanthanides with some substituted sulphonic acids. Many workers [8-23] have reported their results on metal-ligand stability constants. Bodkhe et al [24] have reported the metal-ligand stability constants of some  $\beta$ -diketones. Tekade et al [25] investigated stability constants of some substituted pyrazolines, isoxalline and diketone. Speciation of binary complexes of Ca (II), Mg (II) and Zn (II) with L-glutamic acid in DMSO-water Mixtures has been studied [26]. Thakur et al [27,28] have studied in influence of ionic strength of medium on the complex equilibria of substituted

hydroxy-1-3-propanediones with Cr(III) and La(III) metal ions and Metal-ligand stability constants of Th(III), Sm(III), Nd(III) and Pr(III) metalion complexes with 2-mercapto-4-substituted phenyl-6-substituted phenyl pyrimidines at 0.1 M ionic strength pH metrically . Narwade et al [29] have investigated the Metal-ligand Stability Constants of Cu (II) Complexes and Measurement of Viscosity, Refractivity Index with some substituted Pyrazoles and Diketones at 0.1M Strength. Shivaraj et al [30] have studied formation constants and thermodynamic parameters of bivalentmetal ion complexes with 3-amino-5-ethyl isoxazole Schiff bases and N, N; N, O and O, O donor ligands in solution. Recently Thakur et al [31, 32] have studied The Influence of dielectric constants of medium on the complex equilibria of substituted hydroxy-1, 3-propanediones with Cr (III) metal ions and Studies on Interaction Between Cu (II), Cr (II) and Ni (II) Metal Ions At 0.1 M Ionic Strength pH metrically.

In present work an attempt has been made to study the interactions between Cu (II), Cr (II), Nd (III) and Pr (III) and substituted hydroxy Chalcones at 0.1 M ionic strength, pH-metrically in 70 % dioxane water mixture.

### EXPERIMENTAL SECTION

The chemicals used in the present work were of AR grade. Substituted hydroxy Chalcones (ligand 1 & 2) were synthesized by literature method in laboratory and their purity was checked by IR, NMR and M.P. techniques before used. The solutions of ligands were prepared in purified 70 % dioxane-water mixture and standardized by pH metric technique.

Systronic microprocessor based instrument with accuracy  $\pm 0.01$  units with glass and saturated calomel electrode as used for the titrations. It was calibrated by buffer solution of pH 7.00 and 9.20 at  $28 \pm 0.1$  °C, before processing the titrations.

Titrations were carried out in an inert atmosphere by bubbling a constant flow of nitrogen gar.

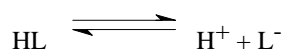
The experimental procedure involved the titrations of:

- i) Free acid  $\text{HClO}_4$  (0.01 M)
- ii) Free acid  $\text{HClO}_4$  (0.01 M) and ligand ( $20 \times 10^{-4}$  M)
- iii) Free acid  $\text{HClO}_4$  (0.01 M) and ligand ( $20 \times 10^{-4}$ ) and metal ion ( $4 \times 10^{-4}$  M) against standard NaOH solution.

The ionic strength of all the solutions was maintained constant (0.1 M) by adding appropriate amount of  $\text{NaClO}_4$  solution. All the titrations were carried out in 70 % dioxane-water mixture and the reading were recorded for each 0.1 ml addition. The graphs of volume of alkali (NaOH) against pH were plotted.

### RESULT AND DISCUSSION

The extent of deviation may be the dissociation of -OH group. Substituted hydroxy Chalcones may be considered as a monobasic acid having one replaceable  $\text{H}^+$  ion from phenolic -OH group and can be represented as



The titration data were used to construct the curves [acid curve (A), acid + ligand curve (A+L) and acid + ligand + metal ion curve (A+L+M)] between volumes of NaOH against pH.

The proton-ligand formation number  $n_A$  were calculated by Irving and Rossotti expression (Table1)

$$\pi_A = \frac{(E_0 + N)(V_2 - V_1)}{(V_0 + V_1) T_L^0} \dots(1)$$

where  $g$  denotes the number of dissociable protons,  $N$  is the concentration of sodium hydroxide ( $0.142 \text{ mol.dm}^{-3}$ ),  $(V_2 - V_1)$  is the measure of displacement of the ligand curve relative to acid curve, where  $V_2$  and  $V_1$  are the volume of alkali added to reach the same pH reading to get accurate values of  $(V_2 - V_1)$ : the titration curves were drawn on an enlarged scale:  $E^0$  and  $T_L^0$  are the resultant concentration of perchloric acid and concentration of Ligand, respectively.  $V_0$  is the initial volume of reaction mixture ( $50 \text{ cm}^3$ ). Proton-Ligand stability constant  $pK$  values (Table 1) of Ligand were calculated by algebraic method point wise calculation and also estimated from formation curves  $n_A$  Vs pH (Half integral method) by noting pH at which  $n_A = 0.5$  [Bjerrum 1957].

Metal-Ligand stability constants ( $\log k$ ) (Table 2&3) were determined by the half integral method by plotting  $n$  Vs  $pL$ . The experimental  $n$  values determined using expression

$$\bar{n} = \frac{(E_0 + N)(V_3 - V_2)}{(V_0 + V_2) T_m^0} \quad \dots(2)$$

Where  $N$ ,  $E_0$ ,  $V_0$  and  $V_2$  have same significance as in equation (1),  $V_3$  is the volume of NaOH added in the metal ion titration to attain the given pH reading and  $T_M^0$  ( $4 \times 10^{-4} \text{ mol dm}^{-3}$ ) is the concentration of metal ion in reaction mixture.

**Table 1: Proton-Ligand stability constants (pK)**

Sr. No.	System	pK	
		Half Integral method	Pointwise Calculation
1.	$L_1$ : 1(2'-hydroxy-5'-methylphenyl)-3-phenyl Chalcone ( $L_1$ )	3.2810	3.2436
2.	$L_2$ : 1(2'-hydroxy-5'-methylphenyl)-3-(4'-methoxyphenyl)-Chalcone ( $L_2$ )	5.7321	5.7201

**Table 2: Metal-ligand stability constants (log K)**

System	Metal Ligand Stability Constants	
	$\log K_1$	$\log K_2$
Cu(II)- ligand - 1	3.8177	1.45
Cr(II) - ligand - 1	3.773	2.763
Nd(III) - ligand - 1	3.687	1.691
Pr(III) - ligand - 1	3.897	2.154
Cu(II) - ligand - 2	5.984	1.661
Cr(II) - ligand - 2	5.653	3.482
Nd(III) - ligand - 2	6.502	1.875
Pr(III) - ligand - 2	5.409	2.899

**Table 3: Metal-ligand Stability Constants (log K)**

System	Metal Ligand Stability Constants	
	$\log K_1 - \log K_2$	$\log K_1 / \log K_2$
Cu(II)- ligand - 1	2.0677	2.632
Cr(II) - ligand - 1	1.015	1.36
Nd(III) - ligand - 1	1.996	2.180
Pr(III) - ligand - 1	1.743	1.809
Cu(II) - ligand - 2	4.324	3.604
Cr(II) - ligand - 2	2.171	1.623
Nd(III) - ligand - 2	4.627	3.467
Pr(III) - ligand - 2	2.51	1.865

### CONCLUSION

From the titration curves, it is observed that the departure between (acid + ligand) curve and (acid + ligand + metal) curve for all systems started from pH = 2.5 this indicated the commencement of complex formation. Also change in colour from yellow to brown in the pH range from 3.5 to 9.0 during titration showed the complex formation between metal and ligand.

The order of pK values of ligands is found to be as

pK ligand (L<sub>2</sub>). > pK ligand (L<sub>1</sub>).

The increment in pK value of ligand (L<sub>2</sub>) is attributed to presence of electron donating –OCH<sub>3</sub> group.

From the table 2 and 3, it is observed that sufficiently large difference between log K<sub>1</sub> and log K<sub>2</sub> values indicates the stepwise formation of complex between metal ion and ligand. The values of log K<sub>1</sub> and log K<sub>2</sub> (table 2) for Cu (II)-L<sub>2</sub>, Cr (II)-L<sub>2</sub>, Nd (III)-L<sub>2</sub> and Pr (III)-L<sub>2</sub> complexes are comparatively higher than Cu (II)-L<sub>1</sub>, Cr (II)-L<sub>1</sub>, Nd (III)-L<sub>1</sub> and Pr (III)-L<sub>1</sub> complexes. It indicates that Cu (II), Cr (II), Nd (III) and Pr (III) forms more stable complexes with ligand (L<sub>2</sub>) than complexes with ligand (L<sub>1</sub>).

The higher value of ratio (log K<sub>1</sub> / log K<sub>2</sub>) for Cu (II) and Nd (III) ligand (L<sub>1</sub> and L<sub>2</sub>) complexes indicate the more stable stepwise complex formation as compare to Cr (II) and Pr (III) complexes.

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